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NMR INVESTIGATION OF FILLER EFFECTS OF γ IRRADIATION IN POLYURETHANE ADHESIVES

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Introduction

Polyurethane and polyester elastomers have been used for decades in a wide variety of applications, from seat cushion foams to prosthetic materials to high performance adhesives.¹ Adiprene LW-520 is a polyurethane-based adhesive used in a number of U.S. Department of Energy applications. Several investigations have been performed to determine aging properties of polyurethanes. For example, ^1H nuclear magnetic resonance (NMR) relaxation times have been shown to be sensitive to thermal degradation in polyurethanes.^{2,3} Detailed information about the exact nature of the oxidative thermal degradation in related materials has also been obtained via ^{17}O and ^{13}C NMR, with additional insight into morphological changes being obtained using ^1H spin diffusion experiments.⁴ Radiation has also been shown to change the physical and mechanical properties of the polymers;⁵ in fact many polyurethanes are cured using radiation to affect the isocyanate and free radical reactive groups, thus controlling the properties such as thermal or solvent resistance.

We have studied the aging of Adiprene polyurethane adhesives in the presence and absence of oxygen while exposed to ionizing radiation by a number of NMR and mechanical testing methods. Solution state ^1H and ^{13}C NMR experiments have been used to investigate chemical speciation changes occurring as a function of aging environment. The changes observed in these methods were relatively subtle and difficult to distinguish by visual inspection alone. To aid in the identification of degradation signatures, we applied Principle Component Analysis (PCA) methods which provide insight into the dependence of degradation pathways on the environmental aging conditions. ^1H solid state spin-echo relaxometry and ^1H multiple quantum (MQ) NMR have been used to provide bulk and network-specific insight into the change in mechanical properties of the material as a function of aging. NMR results have been compared to DMA methods to gain additional insight.

Finally, Diffusion Ordered Spectroscopy (DOSY) was used to investigate differences in aging mechanisms as a function of radiation and filler (Cab-O-Sil) content. DOSY involves the use of pulse field gradients to extract information about translational motion from the NMR data.⁶ In these two-dimensional experiments, the amplitudes of the pulsed field gradients are incremented and the data is transformed to project traditional chemical shift data in the direct dimension and diffusion constants in the indirect dimension instead of a usual NMR spectrum. DOSY has been used to determine diffusion constants in multicomponent mixtures^{6,7} and has proven useful in the polymer community by its use in molecular weight & size distributions of polymer mixtures.^{8,9}

Experimental

Materials. Adiprene LW520 is an isocyanate prepolymer of HyleneW and polytetramethylene ether glycols available from Uniroyal. Unfilled samples were prepared using 14 phr XU-205, mixed for two minutes and centrifuged for five minutes. The components were mixed in ~15% relative humidity conditions and cured at room temperature. Filled samples were prepared in the same manner using 32 parts LW520, nine parts Cab-o-Sil, and seven parts XY-205. Filled and unfilled samples were irradiated in both air and nitrogen atmospheres with doses of 1, 5, 10, and 25 MR.

NMR. ^1H spin echo experiments were performed as previously reported.¹⁰ Multiple quantum NMR experiments were performed using the refocused multiple quantum excitation and reconversion pulse sequence described elsewhere.¹¹ Experiments were performed at 400.13 MHz on a Bruker Avance 400 spectrometer using a Bruker TBI (HCX) 5mm probe. High resolution solution state spectra for PCA analysis were performed at 500.09 MHz on a Bruker Avance 500 MHz spectrometer using a 5 mm TBI probe equipped with pulsed field gradients along the Z axis for use in DOSY experiments.

Results and Discussion

Spin echo NMR data were obtained on the series of irradiated samples and showed minimal changes in the relaxation rate $1/T_2$, which has been previously correlated to the crosslink density, as a function of dose. A slight increase in the relative stiffness was observed in the filled sample irradiated at

high doses in an oxygen-rich environment. Previous studies have shown however, that T_2 values can provide useful information about bulk properties of the polymer but when viewed alone cannot provide network-specific information that would reveal valuable information about structural modifications and changes in segmental dynamics. For comparison with the NMR data, the filled and unfilled irradiated samples were analyzed by Dynamic Mechanical Analysis. The DMA experiments showed a distinct change in storage modulus is observed with radiation dose, yet the dose dependence is opposite in the filled and unfilled samples. The unfilled sample shows a decrease in storage modulus with dose, though the 25 MR sample has a higher modulus than the 10 MR sample. Conversely, the filled sample displays an increase in storage modulus with dose.

For a preliminary understanding of network behavior, two dimensional multiple quantum NMR experiments were performed on the samples and the results for the pristine and irradiated filled Adiprene are shown in Figure 1. In these 2D plots, the normal NMR spectrum appears along the diagonal, while the appearance of off-diagonal peaks in the 25 MR sample indicates homonuclear residual dipolar coupling interactions between the hard segment containing the aromatic groups and the soft segment containing the aliphatic region of the material. The MQ NMR experiments performed on the filled and unfilled adiprene indicated a stiffening of the polymer due to the stronger MQ interaction with dose. The unfilled adiprene showed a small increase in the rate of MQ buildup and a slight broadening of the diagonal on the 2D MQ spectra. The broadening of the diagonal was significantly less severe in the unfilled adiprene samples, suggesting not only increasing polymer-filler interactions with radiation but a strong competition between radiation induced crosslinking and filler bonding mechanisms. Previous studies of filled silicone elastomers have similarly suggested that radiation not only resulted in crosslinking of the polymer network, but a decrease in molecular motion due to covalent bonding to the filler surface was indicated.¹²

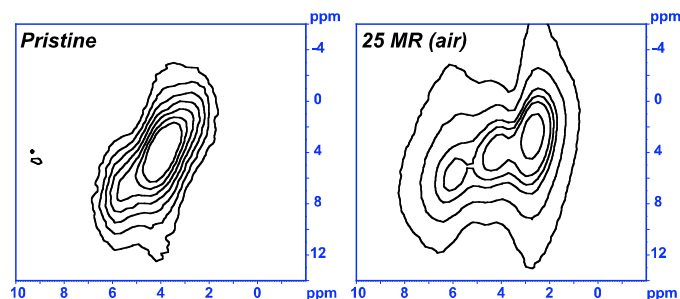


Figure 1. 2D multiple quantum NMR spectra of filled irradiated Adiprene LW-520.

In order to elucidate the exact nature of the degradation, high resolution NMR experiments were performed on CD_2Cl_2 solvent extraction of the soluble portion was performed. Principle component analysis (PCA) was used to analyze the effects of irradiation. Figure 2 displays PCA charts showing distinct groupings of pristine, irradiated filled, and irradiated unfilled samples. The clear separation between the filled and unfilled samples indicates a dependence of the degradation mechanism on the filler.

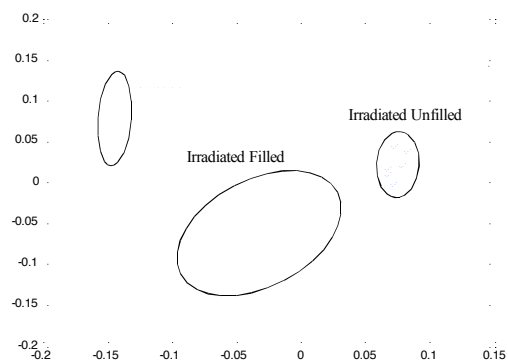


Figure 2. PCA plot of irradiated Adiprene LW520.

To further understand the dependence of aging mechanisms on filler content, diffusion ordered NMR spectroscopy (DOSY) experiments were performed on the solvent extractions. Figure 3(a) shows representative DOSY plots of unfilled pristine sample and one irradiated to 25 MR in air. In Figure

3(b), the distributions of diffusion constants as a function of aging are shown. The appearance of a component with a slower diffusion constant is apparent with increasing dose, particularly in the unfilled samples. These results are consistent with radiation-induced crosslinking, which would produce bulkier, less mobile products. In the filled Adiprene, the filler is evident in the pristine sample as demonstrated by the component with a slower diffusion time, a signal that is not present in the unfilled sample. The filled samples show a more complex effect of the radiation, with slower components growing in at medium doses but disappearing with higher doses. This could be indicative of competing interactions between crosslinking mechanisms and polymer-filler interactions. Interestingly, the faster components in the pristine and low-dose samples having diffusion constants around 10^{-8} to $10^{-8.5}$ m²/sec nearly disappear at higher doses, being entirely replaced with slower components. This would be consistent with a covalent bonding interaction between the network chains and the polymer filler, as indicated in the MQ NMR experiments. More work is currently underway to determine the exact nature of the degradation and the effects of the filler in the adhesive.

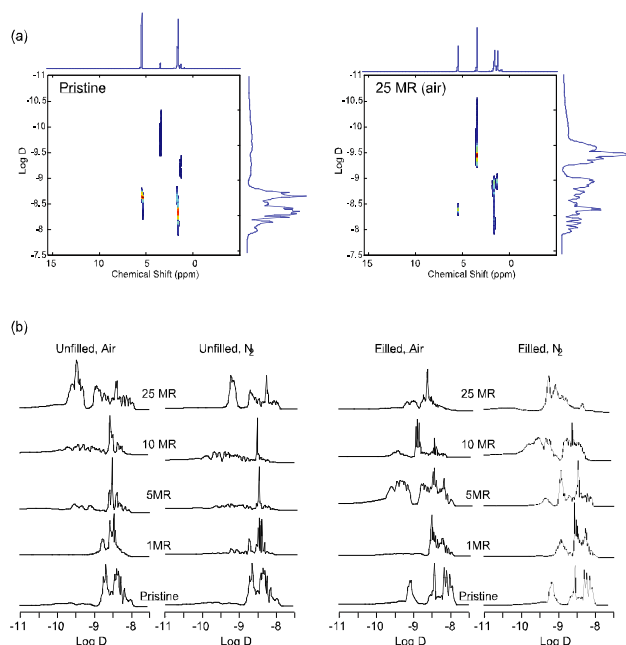


Figure 3. (a) DOSY spectra of unfilled Adiprene LW-520; (b) Diffusion coefficient distributions of unfilled and filled irradiated Adiprene LW-520.

Conclusions

The effects of radiation on filled and unfilled Adiprene LW-520 was investigated with NMR spectroscopy. ¹H spin-echo and MQ NMR revealed slight changes in bulk mechanical properties as a function of irradiation, which was confirmed with DMA analysis. Interestingly, a dependence of the filler content was observed in the aging mechanism. The filler dependence was investigated using principal component analysis to identify common aging mechanisms and diffusion ordered spectroscopy to investigate the changes in diffusion constants and thus translational motional properties of the polymer as a function of aging. It was found that the unfilled Adiprene LW-520 undergoes radiation-induced crosslinking in both oxygen free and oxygen rich environments. Multiple degradation mechanisms exist in the filled polymer, including possible crosslinking and polymer-filler interactions. Work is continuing to provide more insight into the exact nature of these interactions.

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